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 N_2H_4 and $CH_3N_2H_3$ on Si(111)-7x7

by

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The Adsorption and Thermal Decomposition
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Abstract

The adsorption and thermal decomposition of N_2H_4 and $\text{CH}_3\text{N}_2\text{H}_3$ on $\text{Si}(111)\text{-}7\times 7$ were investigated using XPS, UPS and HREELS in the 120-1350 K surface temperature range. Both molecules were partially dissociated into N_2H_x or $\text{CH}_3\text{N}_2\text{H}_x$ ($x=2,3$) species with the N-N bond parallel or nearly parallel to the surface as they adsorbed on the surface at 120 K, especially at lower dosages (e.g., < 0.2 L) and more so for N_2H_4 than $\text{CH}_3\text{N}_2\text{H}_3$. This was evidenced by the appearance of the Si-H vibration at 255 meV in the HREEL spectra and by the relatively larger FWHMs of the N_{1s} XPS and the n^+, n^- molecular UPS peaks. When a ~ 0.4 L N_2H_4 or $\text{CH}_3\text{N}_2\text{H}_3$ dosed sample was annealed to ~ 500 K, significant desorption of the molecules occurred as well as further dissociation of the N-H bonds. Above ~ 600 K, the N-N bond began to break leading to the formation of NH_x ($x=1,2$) species for both molecules. At ~ 730 K, the C-N bond dissociated to form CH_x on the surface in the case of $\text{CH}_3\text{N}_2\text{H}_3$. Further annealing of the sample caused complete cracking of the N-H and C-H bonds until Si_3N_4 or a mixture of Si-nitride and Si-carbide were formed for N_2H_4 or $\text{CH}_3\text{N}_2\text{H}_3$, respectively.

1. Introduction

The direct thermal nitridation of Si substrates using hydrazine (N_2H_4) or any of its alkyl derivatives (e.g., methyl hydrazine, $\text{CH}_3\text{N}_2\text{H}_3$) to produce thin insulating films has been studied and/or patented by a number of investigators [1-4]. However, other than for macroscale information, very little has been published about these potential nitridants regarding the reaction mechanism under various conditions of sub-monolayer coverage and temperature. Thus, considering the fundamental and technological nature of such processing and the recently increased interests in the Si-nitridation process [5-21], a more thorough investigation is important and necessary.

Previous Si-nitridation studies using N_2H_4 as the N source showed that it was a more efficient nitridant and could be effectively used at temperatures lower than NH_3 [1-3] due to its lower energy requirements for dissociative adsorption (i.e., 71 kcal/mole for N-N bond cleavage in N_2H_4 [22] versus 110 kcal/mole for breaking the N-H bond in NH_3 [23]). Using X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), it was shown that similar nitrides were produced and the kinetics were such that a fast initial surface adsorption was followed by a slower diffusional process. Furthermore, it is noted that N_2H_4 has been used in co-deposition schemes involving silanes (e.g., SiH_4 , Si_2H_6 , etc.) in the production of Si_3N_4 [24-28].

The catalytic decomposition of N_2H_4 on metallic surfaces has also been studied under ultra-high vacuum (UHV) conditions [29,30], because N_2H_4 was considered to be the intermediate in the N_2 fixation process. Although having only a cursory relationship to the present work regarding Si-nitridation, these studies do provide a good background with which to compare the characteristics of N_2H_4 adsorption on Si substrates.

With regard to the potential use of alkyl hydrazines (e.g., $\text{CH}_3\text{N}_2\text{H}_3$) as Si nitridants, these authors have been unsuccessful in uncovering any relevant

information other than a few broad statements in patented documentation concerned with either direct thermal nitridation [4] and/or photo-initiated co-deposition reactions with silanes [26]. However, it is noted that the inclusion of the alkyl group makes it interesting because of its potential for C deposition within the prepared nitride. Determining the extent of C-contamination in the prepared nitride may shed light on its overall effectiveness as a nitridant.

In view of the limited available information on the use of hydrazine or its alkyl derivatives in Si-nitridation and in order to compare the present reaction mechanism investigation, it is worthy to consider a number of other surface studies on Si-nitridation using various nitridants; these include the interaction of NH_3 with porous Si [5], NH_3 on Si(111) [6-11] and Si(100) [12-15], N_2^+ on Si(111) [16], N on Si(111) [11,17] and Si(100) [11], NO on Si(111) [9,10,18] and Si(100) [19], and, more recently, HN_3 on Si(110) [20] and Si(111) [21].

Briefly, in the above cases of H-containing nitridants [1-3,5-15,20,21], it is generally agreed that H-adatoms passivate the Si surface at temperatures below ~800 K following dissociative adsorption; above this temperature, desorption of H takes place with the resulting formation of a variety of proposed Si_xN_y structures beginning with a near planar or deformed planar Si_3N [17,18]. For the other nitridants, a similar SiN structure has been proposed to form on the Si surface in the 600-800 K temperature range. At higher temperatures ($T_s > 1300$ K), the Si_3N structure is thought to convert to Si_3N_4 through surface reconstruction processes involving the interdiffusion of Si and N atoms.

In the present investigation, the adsorption and thermal decomposition mechanism of N_2H_4 and $\text{CH}_3\text{N}_2\text{H}_3$ on the Si(111)-7x7 surface over the 120-1350 K temperature range has been studied under sub-monolayer conditions using XPS, ultraviolet photoelectron spectroscopy (UPS), and high-resolution electron energy loss spectroscopy (HREELS).



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2. Experimental Procedures

The experiments were carried out in a custom-made UHV system (Leybold, Inc.) schematically shown in Figure 1. The system is composed of two chambers, one for deposition and the other for surface analysis, separated by a specially designed metal compression seal. Samples can be transferred between sample rods through two independent drive systems and a magnetically operated sample transfer arm.

The surface analysis chamber is separated into two main compartments. One compartment is equipped with AES, XPS (Al $K_{\alpha 1, \alpha 2}$ at 1486.6 eV), and UPS (He II at 40.8 eV), all utilizing a 180° hemispherical electrostatic condenser analyzer for charged particle detection. The second compartment, shielded with μ -metal except for two 10-cm holes allowing for the sample drive system, is equipped with HREELS. The chamber is pumped to a working pressure of 5×10^{-10} Torr through the use of a TMP, liquid nitrogen cold trap, titanium sublimation pump, and an ion pump.

Si(111) single crystal surfaces were cut from 2" wafers (10 Ω -cm, P-doped, Virginia Semiconductor) into 1.5×1.0 cm² samples. After boiling in ~5% HF and rinsing with distilled-deionized H₂O, the samples were suspended between two Ta clips and repeatedly annealed to $T_s > 1520$ K until no C, N, O, or other impurities could be detected by AES, XPS, and/or HREELS. The most sensitive method was apparently HREELS which would produce a band at ~110 meV if any C impurities were present. The sample thus prepared exhibited a very reproducible 7x7 low energy electron diffraction (LEED) pattern indicating the desired starting point for the adsorption experiments.

Resistive heating was accomplished by utilizing a standard DC power supply (Hewlett Packard, Model 6012B). Above ~925 K, a two color pyrometer (Capintec, "Hot Shot") was used for temperature measurements; below ~925 K, temperatures

were estimated by measuring the sample resistance and extrapolating from the higher temperature/resistance calibration curves for each individual sample.

The sample was dosed by back filling the chamber to $\sim 3 \times 10^{-9}$ Torr with dosages being estimated according to the ion gauge readings without further calibration for the different gases. The residual gas, which could not be immediately evacuated, could further dose up to ~ 0.1 Langmuir ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr-sec}$) onto the surface according to a series of time-dependent N_{1s} XPS signal integrations following a measured dose; this additional dosage correction was not included in our later reported dosage levels.

Due to the relatively poor signal-to-noise ratio in some of the XPS spectra, especially the C_{1s} signals at higher annealing temperatures, the XPS data were used only for qualitative purposes. For the UP spectra, the reference energy $E_F = 0 \text{ eV}$ was referred to the well known S_1 , S_2 , and S_3 Si(111)- 7×7 surface states located at $\sim E_F$, -0.8 , and -1.8 eV , respectively [31,32].

In the HREELS experiments, an electron beam having a primary energy of $E_P = 5 \text{ eV}$ and a resolution of $\sim 8 \text{ meV}$, as measured by the full-width-at-half-maximum (FWHM) in the straight through geometry, was used. After scattering from the clean and dosed Si(111) surfaces, the FWHM of the elastic peak usually increased to $\sim 14 \text{ meV}$.

Both hydrazine (98 %) and methyl hydrazine (99 %) were obtained from Aldrich Chemical Co.. These compounds, which invariably contain water as an impurity, were dried over calcium oxide (99.995 %, Aldrich) for a prolonged period of time before use.

3. Results and Discussion

Gas phase hydrazine (N_2H_4) and methyl hydrazine ($\text{CH}_3\text{N}_2\text{H}_3$) molecules are believed to exist in the gauche conformation, i.e., the two N groups are rotated approximately 90° with respect to one another to minimize coplanar repulsion of the

lone electron (e^-) pairs on the N atoms [33,34]. However, upon adsorption to surfaces, this configuration may change, the N-N bond may have various orientations relative to the surface plane, or it may even dissociate due to its interactions with the surface.

3.1. XPS

3.1.1. N_2H_4 / Si

Figure 2 shows a series of N_{1s} XPS spectra for N_2H_4 on a Si(111)-7x7 surface at 120 K and then annealed at the indicated temperatures and cooled back down to 120 K prior to recording the data. When ~ 0.2 L N_2H_4 was adsorbed on the surface, the binding energy (B.E.) of the N_{1s} XPS peak appeared at 400.0 eV having a FWHM of ~ 2.3 eV. As the dosage was increased to ~ 0.4 L, a shift to 400.3 eV and a FWHM reduction to ~ 1.8 eV were noted. A FWHM of ~ 1.8 eV was also found for N_2H_4 adsorbed on Fe(111) surfaces at 126 K, where N_2H_4 was believed to be molecularly adsorbed in a "side on" geometry because "end on" adsorption would give rise to a much wider FWHM (~ 3.5 eV) and could even be resolved into two peaks in some cases due to the different chemical environments of the two N atoms as discussed in detail by Grunze [29]. Thus, our observation of ~ 2.3 eV FWHM at ~ 0.2 L coverage indicates a "side on" adsorption geometry of the molecules, but with some environmental differences between the two N atoms due mainly to the partial dissociation of N-H bonds as evidenced by the Si-H stretching vibration (ν_{Si-H}) band in the HREEL spectra and by the broader n^+n^- UPS peak obtained under essentially identical conditions (see later discussion). As the dosage was increased the spectrum became dominated more with parent molecular features. This is reasonable considering at relatively high coverage there is less chance of dissociation due to the lack of active surface sites. Roughly speaking, if the "side on" adsorption geometry is assumed, each molecule would require at least three adjacent surface sites for the dissociation of one N-H bond. The slight shift of the peak position is also indicative of

the presence of N_2H_x ($x=2,3$) species on the surface. As discussed by Grunze [29], the formation of H-bonds at relatively high coverages would tend to stabilize the N_{1s} e^- in N_2H_4 , and thus would also cause the peak shifting.

When the ~ 0.4 L N_2H_4 dosed sample was annealed to ~ 500 K, a 60-70% decrease in the overall intensity of the N_{1s} XPS signal occurred. The resulting peak was similar to that of the ~ 0.2 L dosed sample but with an even broader FWHM (~ 2.8 eV) showing more contribution from lower B.E. states. At ~ 600 K, a smaller yet broader peak at 399.0 eV was observed. Since N_2H_4 and NH_3 have the same B.E. when adsorbed on both the $\text{Si}(111)\text{-}7\times 7$ and $\text{Fe}(111)$ surfaces, it seems reasonable to assume that similar B.E.s would also exist for N_2H_x ($x=2,3$) and NH_x ($x=1,2$) species as well. Therefore, this peak which is slightly higher in B.E. as compared to those of NH (398.5 eV) or NH_2 (398.8 eV) species on Si surfaces [11,14], is assigned mostly to the presence of N_2H_x ($x=2,3$); however, partial contribution due to NH_x ($x=1,2$) species formed from the cleavage of the N-N bond cannot be ruled out.

Annealing the sample to ~ 650 K shifted the 399.0 eV peak to 398.7 eV and reduced its intensity while the growth of a second peak occurred at 397.2 eV. At ~ 770 K, the 398.7 eV peak nearly disappeared while the peak intensity at 397.2 eV was further enhanced. The latter peak, also observed for Si-N species on different Si surfaces [14], confirmed the cracking of the N-N bond as well as further cracking of NH_x species. These results are also consistent with our HREELS and UPS studies over the same temperature range.

Continued annealing to temperatures up to ~ 1350 K caused only a minor peak shift to higher B.E.s indicating the formation of different Si-N bonds, e.g., $\text{Si}_3\text{N} \rightarrow \text{Si}_3\text{N}_4$ species. Such a shift was also observed when NH_3 dosed Si surfaces were annealed at higher temperatures [10,14,15]. The small but noticeable increase in the N_{1s} XPS peak intensity at higher annealing temperatures is most likely due to the readsorption of N-containing species desorbed from the surrounding surfaces of the sample holder

which are also warmed during the sample annealing procedure as well as residual gases in the chamber. Such readsorption would also tend to produce a N_{1s} peak skewed towards higher B.E.s since the readsorbed species could be incompletely dissociated. This readsorption phenomenon has also been reported elsewhere [15].

3.1.2. $CH_3N_2H_3$ / Si

Figures 3a and 3b show a series of N_{1s} and C_{1s} XPS spectra, respectively, obtained similarly to those in Figure 2. When ~ 0.15 L $CH_3N_2H_3$ was dosed on to Si(111)-7x7 at 120 K, a N_{1s} XPS peak at 400.1 eV having a FWHM of ~ 1.9 eV with a lower B.E. tail was observed. As the dosage was increased to ~ 0.4 L, the peak shifted to 400.4 eV with a FWHM of ~ 1.8 eV. The corresponding C_{1s} XPS results showed peaks at 286.8 (not shown here) and 286.9 eV for ~ 0.15 and ~ 0.4 L $CH_3N_2H_3$ coverages, respectively.

The similarity of the N_{1s} XPS for both N_2H_4 and $CH_3N_2H_3$ suggests that there is little effect on the N_{1s} electrons upon the replacement of a H atom with a CH_3 group. In support of our HREELS results to be discussed later, the narrower FWHM at relatively lower dosage for $CH_3N_2H_3$ compared to that for N_2H_4 indicates that there is less dissociation of N- CH_3 or N-H to form Si-H upon adsorption.

When the ~ 0.4 L dosed sample was annealed at ~ 500 K, the N_{1s} peak decreased in intensity, shifted to 400.2 eV, and broadened to give a FWHM of ~ 2.6 eV; at ~ 600 K, a very broad peak centered at 399.1 eV resulted. This is virtually the same as for N_2H_4 above; however, the larger tail at higher B.E.s for $CH_3N_2H_3$ as compared to N_2H_4 again suggests less dissociation of the $CH_3N_2H_3$ molecules. Meanwhile, the C_{1s} XPS also shifted to 286.5 and 286.0 eV at ~ 500 and ~ 600 K, respectively. These relatively large shifts in the C_{1s} peak are probably due to the breaking of the N-H bond in closest proximity to the CH_3 group as well as some of the N-N and, possibly, C-H

bonds at ~600 K; furthermore, if C-H bonds are broken, the possible formation of Si-C bonds may also cause some shifting in the C_{1s} XPS peak position.

Annealing up to ~700 K produced little changes in the C_{1s} XPS; on the other hand, significant changes in the corresponding N_{1s} XPS structure occurred. At ~650 K, a broad peak was located at 397.6 eV indicating cleavage of the N-N bond and further cracking of NH_x species; the tail at higher B.E.s was due to less-dissociated species. At ~700 K, only one peak centered at 397.6 eV was clearly evident.

Annealing the sample to ~730 and ~770 K caused the N_{1s} XPS peak to shift to 397.3 eV while the C_{1s} XPS exhibited a new peak at ~284.2 eV and one single peak at 283.1 eV for these respective temperatures. This dramatic change in the C_{1s} XPS at ~730 K strongly suggests the breaking of the C-N bond to form SiCH_x species and the continued shifting of the peak at ~770 K is probably due to additional cracking of the C-H bonds.

Higher temperature annealing induced similar changes in the N_{1s} peak as those for N₂H₄ above. The C_{1s} peak shift to 283.0 eV was due to the complete removal of N-H and C-H bonds which, according to our HREELS measurements, happened at T_s > 1000 K with the resultant formation of Si-nitride and Si-carbide, or a mixture thereof. Porte [35] observed a C_{1s} B.E. of 282.9 eV in SiC. The earlier discussed readsorption effect is also present to some degree.

3.2 UPS

3.2.1. N₂H₄ / Si

Figures 4a and 4b show a series of UP spectra for N₂H₄ on Si(111)-7x7. When ~0.2 L N₂H₄ was dosed on the substrate at 120 K, the He II UPS produced two broad peaks centered at 4.7 and 10.8 eV below E_F having FWHMs of ~3.2 and ~3.6 eV, respectively. Comparing this with gas phase UPS results for N₂H₄ [36,37], where two doublet bands were observed with maxima at 9.9 and 10.6 eV below the vacuum level

E_V and at 15.6 and 16.7 eV below E_V having overall FWHMs of ~ 1.7 and ~ 2.8 eV, respectively, these are readily assigned to the n^+, n^- orbitals and the N-N and N-H orbitals, respectively, which are not resolved in our case. Further dosing of ~ 0.2 L N_2H_4 on the sample caused no obvious change of the peak at 10.8 eV, but the peak at 4.7 eV shifted to 5.2 eV with a FWHM of ~ 2.8 eV. These results are consistent with those of Grunze [29] for N_2H_4 on Fe(111) where two unresolved bands at 6.4 and 11.4 eV below E_F having FWHMs of ~ 2.6 and ~ 2.6 eV at lower dosages and 5.8 and 12.0 eV below E_F having FWHMs of ~ 2.7 and ~ 3.6 eV at relatively higher dosages were observed. Recalling the similar N_{1s} XPS effects at lower dosage, the UPS band broadening in the present study again reflected the partial dissociation of N-H bonds which was confirmed in our HREELS results.

When the ~ 0.4 L dosed sample was annealed at ~ 500 K, the resulting UP spectra was basically the same as that of the ~ 0.2 L dosed sample except for a noticeable tail at lower B.E.s for the 10.8 eV peak. The significant decrease in the peak intensities was due to the desorption of some molecules while the lower B.E. tail for the 10.8 eV may indicate further cracking of N-H bonds which is consistent with our N_{1s} XPS results above. It is noteworthy to point out that gas phase N_2H_2 UPS [38] produced four bands at 10.0, 14.4, 15.5, and 16.9 eV. Recall, N_2H_4 yielded 9.9, 10.6, 15.6, and 16.7 eV values [37,38]. Thus, one should expect to have a relatively broader peak at ~ 10.8 eV or a lower B.E. tail if N_2H_2 or N_2H_3 species were to be formed.

Annealing the sample to ~ 650 K caused cleavage of the N-N bond as indicated by the three broad peaks at 3.7, 7.4, and 10.2 eV, which are due to NH_x species on Si surfaces corresponding to N_{2p} (lone e^- pairs) and Si-H, $N_{2p_{x,y}}$ and Si_{3p} , and $N_{2p_{x,y}}$ and Si_{3s} orbitals, respectively. The peaks at around 4, 7, and 10 eV were also observed previously with other N-containing molecules adsorbed on Si surfaces, e.g.,

ND₃ on Si(100) and Si(111) [11], N on Si(100) [11], NH₃ on Si(100) [14], NH₃ on Si(111) [10], and N₂⁺ sputtered on Si(111) [16].

Heating the sample to higher temperatures caused only minor shifting in the peak positions as well as some intensity variations due mainly to additional cracking of NH_x species, desorption of H, and Si₃N-->Si₃N₄ type structural transformations. At ~1350 K, three peaks centered at 4.4, 7.0, and 11.2 eV remained. These are in very good agreement with those of previous pseudo-Si₃N₄ UPS results, especially those with x=0.5 in SiN_x [39], and also in good agreement with the UP spectra of NO or NH₃ on Si(111) after annealing at 1150 K or 1000 K, respectively [9].

A sample prepared by co-dosing Si₂H₆ and N₂H₄ at a 3:1 Si:N ratio ($P_t = 5 \times 10^{-5}$ Torr, 4 hours) on a Si(111) surface at 1000 K also produced three UPS peaks at 4.5, 6.9, and 11.7 eV, but with stronger intensities. This sample had a much thicker overlayer of Si₃N₄ as evidenced by XPS and AES.

3.2.2. CH₃N₂H₃ / Si

When ~0.3 L CH₃N₂H₃ was dosed on Si(111)-7x7 at 120 K (Fig. 5a and 5b), broad bands at 4.4, 9.2, 10.7, and 16.2 eV below E_F were clearly present. If a surface work function of 4.8 eV for Si(111) is taken into account [40], the 4.4, 9.2, and 10.7 eV values compare favorably to the gas phase UPS of CH₃N₂H₃ where three doublets centered at 9.5, 13.8, and 15.8 eV were previously observed [36]. The additional peak at 16.2 eV, corresponding to the C_{2s} orbital, was not shown in the gas phase spectra, however, this was observed at ~15.7 eV in an earlier UPS study of In(CH₃)₃/Si(111) [41] and also by Wen and Rosenberg [42] for CH₃F on Si(111) at ~17 eV. By analogy to the gas phase UP spectra, we have assigned the three peaks at 4.4, 9.2, and 10.7 eV below E_F as due to n⁺ and n⁻, C-H, and N-C, N-H, and N-N molecular orbitals, respectively.

When the sample was annealed to ~500 K, the peak at 4.4 eV shifted to 4.2 eV and a shoulder became apparent on the lower B.E. side of the 9.2 eV peak. These changes, although weaker, are similar to those obtained above for N_2H_4 / Si(111)-7x7 where further cracking of N-H bonds occurred. It is also noted that gas phase UP spectra of CH_3NNH have produced bands at 9.6, 12.9, 13.4, 14.7, 15.6, and 16.7 eV [38] and our observation of the shoulder on the lower B.E. side of the C-H peak at 9.2 eV may suggest the formation of similarly related species.

Annealing at ~650 K caused broadening and shifting to the lower B.E. side of the peaks at 4.2 and 16.2 eV, a significant decrease in the peak at 10.7 eV, and the introduction of a broad peak centered at 8.2 eV which coupled with the C-H peak at 9.2 eV to produce a very broad band spread from 7 to 10 eV. These changes are attributed to the rupture of the N-N bond and some N-H bonds, as evidenced by our XPS and HREELS studies.

Further heating to ~730 K caused the C_{2s} peak to shift from 15.9 to 15.5 eV and the C-H peak to shift from 9.2 to 8.5 eV which should be due to SiCH_x species formed following the cleavage of the C-N bond. Similar C_{2s} and C-H peak shifts to lower B.E.s were also observed for the case of CH_3F on Si(111) when the C-F bond cracked to form SiCH_x species [42]. Additionally, the introduction of a weak peak at 7.2 eV should be due to the formation of SiNH_x species. At ~770 K, the C_{2s} and C-H peaks were almost extinguished and a new peak at 6.8 eV with two shoulders at ~10.7 and ~4.1 eV dominated the spectra. This is very similar to SiN UP spectra (discussed above) indicating the breaking of C-N and C-H bonds, the latter also clearly shown in our HREELS results below.

Annealing to temperatures up to ~1350 K caused only slight changes in the relative intensities as well as minimal shifting of the bands. These subtle effects are most probably due to changes in the Si-N and Si-C structures. The reported UPS of SiC [35] showed three bands at 3.5, 7.0, and 9.8 eV and, in the present study, were

not separated from those due to Si-nitride observed at 4.4, 7.0, and 11.2 eV in the N_2H_4 / Si(111)-7x7 UP spectra above.

3.3 HREELS

3.3.1. N_2H_4 / Si

Figures 6a and 6b show a series of HREEL spectra for ~ 0.3 L N_2H_4 dosed on Si(111)-7x7. When dosed at 120 K, vibrational bands centered at 109, 134, 198, 255, and 411 meV were clearly present. Previous IR or Raman studies [43] on solid N_2H_4 have exhibited bands at 110, 140, 162, 199, 397, and 410 meV corresponding to NH_2 -rocking (ρ_{NH_2}), NN-stretching ($\nu_{\text{N-N}}$), NH_2 -wagging (ω_{NH_2}), NH_2 -deformation (δ_{NH_2}), and NH-stretching (ν_{NH}) vibrations, respectively; in addition, two NH_2 torsional (τ_{NH_2}) vibrations at 50 and 81 meV were also observed.

By analogy to the solid N_2H_4 spectra, we have assigned the observed bands for N_2H_4 / Si(111)-7x7 as shown in Table 1. Of course, the $\nu_{\text{Si-H}}$ band at 255 meV was not present in the solid N_2H_4 spectra. Although rather weak at 120 K, the ω_{NH_2} band at ~ 161 meV became better resolved at ~ 500 K. It is also noted that the τ_{NH_2} vibrations were barely visible in all of our spectra, and the broad band at 109 meV may have some contribution from the $\nu_{\text{Si-NH}_x}$ vibration previously observed at 103 meV [5].

While all other bands were in excellent agreement with those for solid N_2H_4 , the $\nu_{\text{N-N}}$ vibration was red-shifted to a fair degree. This shift implies weakening of the N-N bond through interaction with the surface or it may also be due to the partial dissociation of the N-H bond as evidenced by the presence of the $\nu_{\text{Si-H}}$ vibrational mode. The partial dissociation of the N-H bond may also contribute to the broadening of the $\nu_{\text{N-H}}$ band centered at 411 meV which should be due to the two unresolved symmetric and antisymmetric $\nu_{\text{N-H}}$ vibrations.

IR spectra of N_2H_4 on Ge [44] and HREELS spectra of N_2H_4 on Ni(111) [30] have produced similar results and are also listed in Table 1.

Before proceeding to a discussion about the effect of annealing on the HREEL spectra, it is worthwhile to consider the adsorbate geometry relative to the substrate. Off-specular HREEL spectra shown in Figure 7 are in fair agreement with our earlier N_{1s} XPS and UPS results which suggested a "side on" as opposed to an "end on" adsorption geometry for N_2H_4 on Si(111)-7x7. In the 9° off-specular mode, all molecular vibration bands were only attenuated by less than 5 times as compared to those in the specular mode, while ν_{Si-H} was essentially absent. Further, the 109 meV structure is more attenuated than the other molecular vibrations because of a contribution from the ν_{Si-NH_x} band. In addition, the band near 335 meV which results from the combination of ν_{N-N} at 134 meV and δ_{NH_2} at 199 meV was much more apparent. These effects suggest the molecular vibrations are due to impact scattering and, thus, support the proposed "side on" adsorption geometry.

Furthermore, the ν_{N-N} vibration was much more intense on Ni(111) [30] than on Si(111)-7x7. This difference may suggest that the N-N bond orients differently on the two surfaces, i.e., perpendicular or nearly perpendicular to the Ni(111) surface and parallel or nearly parallel to the Si(111) surface, respectively. In another study involving the adsorption of N_2H_4 on Pt(111) [45], the molecules were also believed to be adsorbed on the surface in the "side on" fashion; additionally, with heat treatment, N-H bonds were noted to break prior to N-N bonds which survived to higher temperatures. It is noted that on the Ni(111) surface, when warmed to 285 K, N_2H_4 dissociated to give desorbed NH_3 with NH remaining attached to the substrate. The behavior of N_2H_4 on Si(111) is quite different as discussed below.

Upon annealing the 120 K adsorbed N_2H_4 / Si(111)-7x7 to ~500 K, there was little noticeable change in the spectra; on the other hand, at ~650 K, several changes were observed. First, the ν_{N-H} band shifted from 411 meV to 421 meV; in addition, the bands at 109, 134, 161, and 198 meV essentially disappeared while a new broad band centered at ~114 meV emerged. These results are consistent with the cracking

of the N-N bond. Finally, a shoulder on the higher energy loss side of the 255 meV peak results from the $\nu_{\text{Si-H}}$ vibration where the Si atoms are back-bonded to N atoms [5,6].

In comparison to other related studies, Tanaka et al. [6] observed bands at 98, 135, 188, and 421 meV for NH_3 on $\text{Si}(111)\text{-}7\times 7$ at 300 K and 76, 100, 188, and 421 meV at 700 K and attributed these mainly to the presence of NH_2 species with some possible contribution from NH species as well, especially at 700K. At 900 K, only two weak bands at 100 and 120 meV were evident indicating the formation of Si-nitride. HREELS studies by Larsson et al.[12] of NH_3 on $\text{Si}(100)\text{-}2\times 1$ produced peaks at 102, 192, and 422 meV for NH_2 species over the 300-800 K temperature range and, at 1100 K, 100 and 128 meV bands due to the formation of Si_3N_4 . Similar observations were noted by Kilday et al. [8] for NH_3 adsorbed on cleaved $\text{Si}(111)\text{-}2\times 1$ at 300 K. Bands at 96 and 430 meV were assigned to adsorbed NH_3 molecules at low dosages; however, new bands at 190 and 255 meV, due to the dissociation of NH_3 , appeared with a corresponding red-shift in the 430 meV band to 420 meV as the dosage was increased.

IR studies of NH_3 on porous Si samples [5] yielded vibrational bands at 103, 190, 420, and 430 meV due to Si-NH_2 species and weaker bands at 95 and 137 meV due to a small population of Si_2NH species over the 300-680 K temperature range. At 680-860 K, Si_3N was formed which exhibited bands at 93, 115, and 135 meV.

In the present study, when $\text{N}_2\text{H}_4/\text{Si}(111)\text{-}7\times 7$ was annealed to ~650 K, a weak band present at 194 meV and a stronger band at 421 meV indicated the presence of NH_2 species. On the other hand, the NH bending vibration ($\beta_{\text{N-H}}$) was not resolved from the broad band centered at ~114 meV. The latter should have contributions from ρ_{NH_2} at ~110meV, Si_3N bands at 93, 115, and 135 meV, and possibly a band at 95 meV due to NH species. This same broad band was also present for HN_3 on $\text{Si}(110)$

at ~110 meV after annealing to ~800 K [20] and its span has been suggested to reflect variations in the binding between Si and N atoms [17].

Annealing the sample to ~700 K produced shifts in the $\nu_{\text{N-H}}$ and $\nu_{\text{Si-H}}$ bands to ~415 and ~260 meV, respectively. The former shift may actually indicate partial $\text{SiNH}_2 \rightarrow \text{Si}_2\text{NH}$ conversion since the corresponding R_3SiNH_2 compounds exhibited $\nu_{\text{N-H}}$ bands at 422 and 431-432 meV which were red-shifted to 415-419 meV in $(\text{R}_3\text{Si})_2\text{NH}$ compounds [46]. However, $\beta_{\text{N-H}}$ was still not resolved from the broad band at ~114 meV. In other studies, clear proof for the existence of a Si_2NH species has been somewhat proximal, especially noting the absence of the weak $\beta_{\text{N-H}}$ band expected at ~145 meV since such a vibration has been shown to exist for $(\text{R}^1\text{R}^2\text{R}^3\text{Si})_2\text{NH}$ molecules from 144 to 146 meV [46]. On the other hand, the decomposition of N_2H_4 on Ni(111) [30] resulted in a band at ~157 meV which was assigned to the $\beta_{\text{N-H}}$ vibration and a N_{1s} XPS study of NH_3 on a Si(111) surface resulted in a B.E. of 387.5 eV which was assigned to the NH species. In our earlier study of HN_3 on Si(110) [20], the NH bending vibration at ~160 meV was also observed. The peak at 262 meV, due to HSiN_x , indicates the further cracking of NH bonds and the forming of the Si-N bond.

Continued annealing of the sample up to ~1000 K nearly caused the complete cleavage of the N-H bonds and the subsequent desorption of H leading to the effective nitridation of the Si surface. At ~1350 K, the broad band at ~120 meV decreased in intensity and separated into four bands centered at 62, 92, 123, and 135 meV. According to Taguchi et al. [19] and Edamoto et al. [17], who observed similar peaks at ~60, ~90, 109, and 130 meV and peaks at 60, 91, 120, and 141 meV, respectively, for NO or N on Si(111) after annealing to $T_s > 1200$ K, these are due to the formation of Si_3N_4 .

3.3.2. $\text{CH}_3\text{N}_2\text{H}_3$ / Si

A series of HREEL spectra for ~ 0.3 L $\text{CH}_3\text{N}_2\text{H}_3$ on Si(111)-7x7 are shown in Figures 8a and 8b. After dosing at 120 K, bands at 140, 181, 367, and 410 meV were clearly visible; these are presented in Table 2 together with previous IR/Raman spectroscopic results for gaseous and liquid $\text{CH}_3\text{N}_2\text{H}_3$ [47]. By analogy to these vibrational studies, we have assigned the peaks at 181, 367, and 410 meV to δ_{CH_3} , $\nu_{\text{C-H}}$, and $\nu_{\text{N-H}}$, respectively. Similarly, the broad band centered at ~ 140 meV is due to a mixture of vibrations, i.e., ρ_{CH_3} , ω_{CH_3} , the skeletal N-N stretch, $\beta_{\text{N-H}}$ vibrations, etc. There is also a noticeable hump at ~ 256 meV due to $\nu_{\text{Si-H}}$, which is more obvious at lower dosages.

It is noteworthy to point out the near absence of any strong NH_2 -group vibrations, namely δ_{NH_2} at 199 meV, ω_{NH_2} at 160 meV, and ρ_{NH_2} at 110-117 meV, and this can be argued as follows. Since the N-H bond strength in the terminal NH_2 -group is only slightly stronger than that of the N-H bond adjacent to the CH_3 -group [48], the near absence of any NH_2 vibrations may suggest that the surface interaction of the CH_3 -group is not negligible. Such a CH_3 -surface interaction would tend to make the C-N-N plane nearly parallel to the surface and, accordingly, the N-H bond adjacent to the CH_3 -group would point outwards from the surface. This would leave one of the H atoms of the terminal NH_2 -group attached to the surface and may or may not lead to the partial decomposition of the NH_2 -group upon adsorption, i.e., the cracking of one N-H bond. The latter is more obvious at lower dosage (c.f. Fig. 9, curve a), and very clear in the case of N_2H_4 where the $\nu_{\text{Si-H}}$ vibration at 255 meV was much stronger (Fig. 6a).

When the sample was annealed at ~ 500 K, there were few spectral changes except for a slight shift to 412 meV from 410 meV and a subtle decrease in the $\nu_{\text{N-H}}$ band. These were probably a result of the further cracking of NH bonds.

Similarly to the N_2H_4 case above, the following changes were noted as the sample was annealed to ~ 650 K. First, the $\nu_{\text{N-H}}$ band shifted from 412 to 422 meV and a shoulder emerged at ~ 110 meV indicating the cleavage of the N-N bond to form SiNH_x ($x=1,2$) and SiNH_xCH_y ($x=0,1$; $y=1-3$) species. In addition, the $\nu_{\text{Si-H}}$ band at 260 meV was significantly enhanced, reflecting the partial yet pronounced cracking of N-H and/or C-H bonds. Furthermore, due to the N-N bond cleavage and the reduction of the ρ_{CH_3} and $\beta_{\text{N-H}}$ modes, the peak at 140 meV red-shifted to 130 meV which correlates well with the C-N stretching vibration as $(\text{CH}_3)_3\text{N}$ has been shown to have a $\nu_{\text{C-N}}$ mode at ~ 129 meV [49].

Upon heating to ~ 770 K, the rupture of the C-N bond was evidenced by the disappearance of the $\nu_{\text{C-N}}$ mode at 130 meV. A significant intensity reduction of the bands at 180, 370, and 422 meV also indicated the further cracking of N-H and C-H bonds. Meanwhile, the enhanced intensity at 117 meV was due to the additional formation of Si- CH_x and Si- NH_x bonds.

Further annealing to higher temperatures resulted in the gradual fading of all bands except for the one at 117 meV which, at ~ 1350 K, became narrower yet stronger in intensity and blue-shifted to ~ 120 meV with a shoulder at ~ 90 meV. These changes at ~ 1350 K were most probably due to the diffusion of N and C atoms into the substrate or outward diffusion of Si to form a mixed, insulating layer of Si-nitride and Si-carbide [6,19].

While in the case of N_2H_4 an 8×8 LEED pattern was observed for the sample annealed to ~ 1350 K, the $\text{CH}_3\text{N}_2\text{H}_3$ sample above exhibited a "quadruplet" LEED pattern. These LEED observations are consistent with those reported by Schrott and Fain [50], i.e., "quadruplet" and 8×8 LEED patterns for Si-nitride, with and without intrinsic C contamination, respectively.

3.4 Laser Radiation Effects at 120 K

In the gas phase photolysis of N_2H_4 [51-54], 193 nm laser radiation has been shown to produce a variety of primary and/or secondary species (e.g., $\text{N}_2\text{H}_4 + h\nu \rightarrow \text{N}_2\text{H}_3 + \text{H}$, $\text{N}_2\text{H}_4 + h\nu \rightarrow \text{NH}_2^* + \text{NH}_2$, etc.). Furthermore, Vinogradov and Firsov [55] determined that the photolysis cross section for the production of excited NH ($A^3\Pi$) and NH_2 (A^2A_1) fragments increased significantly from 300 to 573 K. Additionally, a number of photon-enhanced co-deposition schemes involving N_2H_4 or its organic derivatives and silanes to produce Si-nitride at moderate temperatures have been patented [26,56-59]. With these factors in mind, laser radiation effects have also been briefly investigated in the present work.

N_2H_4 or $\text{CH}_3\text{N}_2\text{H}_3$ dosed Si(111)-7x7 surfaces at 120 K were exposed to 308, 248, and 193 nm excimer laser radiation having a flux of $\sim 10 \text{ mJ/pulse-cm}^2$ and operated at a repetition rate of 20 Hz for 30 minutes. After the radiation exposure, no obvious changes in the corresponding HREEL spectra were observed except the $\nu_{\text{Si-H}}$ vibrational band at 255 meV was almost extinguished indicating the desorption of the adsorbed H species. A typical result is shown in Figure 9 for a $\sim 0.2 \text{ L}$ $\text{CH}_3\text{N}_2\text{H}_3$ dosed Si(111)-7x7 sample exposed to 248 nm excimer laser radiation. There was also a small yet discernable decrease in the $\nu_{\text{N-H}}$ band, which may be due to the further dissociation of N-H bonds as more surface sites became available after the desorption of H. Similar effects were also observed when dosed surfaces were exposed to a Hg lamp or an Al X-ray source. The latter X-ray-induced intensity reduction effects on the $\nu_{\text{Si-H}}$ and ν_{NH_2} peak heights were also observed by Kilday et al. [8] recently in the study of NH_3 on Si(111)-2x1.

In light of the near 650 K thermal requirement for N-N bond rupture as determined in the present investigation and the previously reported temperature effect on the N_2H_4 photolysis cross-section, it is believed that additional photon energy will

substantially reduce this thermal requirement. An investigation on the combined effects of laser radiation exposure and thermal treatment of previously dosed substrates is planned in the near future for N_2H_4 , $\text{CH}_3\text{N}_2\text{H}_3$, and HN_3 on Si(111)-7x7.

4. Conclusions

The adsorption and thermal decomposition reaction mechanisms for N_2H_4 and $\text{CH}_3\text{N}_2\text{H}_3$ in the nitridation of Si(111)-7x7 substrates were studied with XPS, UPS, and HREELS. Both molecules were found to have some N-H dissociation with the N-N bond parallel or nearly parallel to the surface upon adsorption at 120 K, especially at lower dosages and more so for N_2H_4 than $\text{CH}_3\text{N}_2\text{H}_3$. Annealing the dosed surface to ~650 K caused the N-N bond to break as evidenced by the larger N_{1s} XPS peak shift, the intensity decrease in the $\nu_{\text{N-N}}$ vibrational band in HREELS, and the peak shifts in the UP spectra as well. In the case of $\text{CH}_3\text{N}_2\text{H}_3$, the C-N bond started to break at ~730 K, which was indicated by a large shift in the C_{1s} XPS peak and additional changes in the UP and HREEL spectra. Further cracking of N-H and C-H bonds also occurred in the $T_s < 800$ K temperature range. Annealing the surface to higher temperatures resulted in the formation of Si-nitride and a mixture of Si-nitride and Si-carbide in the cases of N_2H_4 and $\text{CH}_3\text{N}_2\text{H}_3$, respectively.

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Table 1. Comparison of the vibrational frequencies of solid N₂H₄ (IR / Raman) and N₂H₄ adsorbed on Ni(111) and Si(111)-7x7. Data given in meV (cm⁻¹).

Mode	Solid N ₂ H ₄ ^a	N ₂ H ₄ / Ni(111) ^b	N ₂ H ₄ / Si(111)-7x7 ^c
ρ_{NH_2}	110 (884)	112 (900)	109
$\nu_{\text{N-N}}$	140 (1126)	133 (1070)	134
ω_{NH_2}	162 (1304)	166 (1340)	162
δ_{NH_2}	199 (1603)	196 (1580)	198
$\nu_{\text{N-H}}$	397 (3200)	391 (3150)	393
	410 (3310)	409 (3300)	411
τ_{NH_2}	50 (405)	42 (340)	
	81 (650)	71 (570)	

a.) Ref. 43

b.) Ref. 30

c.) this work

Table 2. Comparison of the vibrational frequencies for $\text{CH}_3\text{N}_2\text{H}_3$ (gas and liquid) and $\text{CH}_3\text{N}_2\text{H}_3$ / Si (111)-7x7. Data given in meV (cm^{-1}). Data given in meV (cm^{-1}).

Mode	gas (IR) ^a		Liquid (Raman) ^a		on Si(111)-7x7 ^b
$\nu_{\text{N-H}}$	417	(3366)	411	(3316)	410
	416	(3358)	410	(3304)	
	410	(3314)	404	(3258)	
$\nu_{\text{C-H}}$	368	(2967)	367	(2962)	367
	366	(2951)	364	(2938)	
	345	(2784)	345	(2782)	
δ_{CH_3}	183	(1479)	182	(1469)	181
	182	(1465)	179	(1445)	
	180	(1449)	175	(1412)	
ω_{NH_2}	159	(1282)	162	(1305)	
ω_{CH_3}	150	(1210)	149	(1200)	
ρ_{CH_3}	139	(1118)	139	(1122)	
$\beta_{\text{N-H}}$	139	(1124)	141	(1137)	140
Skel. stretch (N-N)	137	(1108)	137	(1104)	
Skel. stretch (C-N)	120	(968)	123	(992)	
ρ_{NH_2}	110	(888)	115	(930)	
$\beta_{\text{N-H}}$	96	(777)	102	(821)	
Skel. bend	53	(425)	55	(447)	
τ_{NH_2}	39	(316)	45	(363)	
τ_{CH_3}	32	(257)	32	(259)	

a.) Ref 47 , b.) this work.

Figure Captions

- Figure 1: Schematic illustration of the experimental UHV apparatus
- Figure 2: N_{1s} XPS spectra for N_2H_4 adsorbed on a Si(111)-7x7 surface at 120 K and annealed at the indicated surface temperatures
- Figure 3a: N_{1s} XPS spectra for $CH_3N_2H_3$ adsorbed on a Si(111)-7x7 surface and annealed at the indicated temperatures
- Figure 3b: C_{1s} XPS spectra for $CH_3N_2H_3$ adsorbed on a Si(111)-7x7 surface and annealed at the indicated temperatures
- Figure 4: He II UP spectra for N_2H_4 adsorbed on a Si(111)-7x7 surface and annealed at the indicated temperatures (Note: for visual clarity, figure is broken into (4a) and (4b))
- Figure 5: He II UP spectra for $CH_3N_2H_3$ adsorbed on a Si(111)-7x7 surface and annealed at the indicated temperatures (Note: for visual clarity, figure has been broken into (5a) and (5b))
- Figure 6: HREEL spectra for N_2H_4 adsorbed on a Si(111)-7x7 surface and annealed at the indicated temperatures (Note: for visual clarity, figure has been broken into (6a) and (6b))
- Figure 7: HREEL spectra of N_2H_4 adsorbed on Si(111)-7x7 taken in (a) the specular and (b) 90° off-specular modes
- Figure 8: HREEL spectra for $CH_3N_2H_3$ adsorbed on a Si(111)-7x7 surface and annealed at the indicated temperatures (Note: for visual clarity, figure has been broken into (8a) and (8b))
- Figure 9: HREEL spectra of ~ 0.2 L $CH_3N_2H_3$ adsorbed on a Si(111)-7x7 surface at 120 K (a) before and (b) after exposure to 248 nm excimer laser radiation.

UHV Gas-Surface Reaction System with Multiple Diagnostics



























